ENAMELS

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ENAMEL WITH THE AVENTURINE EFFECT

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The aventurine effect is detected in chromium- and alkali-containing aluminoboron silicate glass and enamel based on it. The effect of the glass acidity and the ratio of the alkali oxides on the aventurine effect and the size of the crystals in glass and enamel is investigated.

Creation of low-melting decorative enamels for copper and copper alloys is an important and topical problem.

There are currently several known methods for producing aventurine glass used as decorative facing material in construction [1, 2]. As a rule, metallurgical slag is introduced into the composition of such glasses to lower the production cost. However, these glasses have high temperatures of melting (1673 – 1773 K) and heat treatment (1273 – 1573 K) [1], which makes them unacceptable as a base for producing enamels with the aventurine effect.

There are data on aventurine glazes with a high content of Fe_2O_3, Cr_2O_3, and Mn_2O_3 (up to 15 – 30 wt.%). This is an old method for decoration of ceramic articles. In the course of slow cooling of articles after firing, the glaze crystallizes and produces decorative effects similar to natural aventurine [3, 4]. Such glasses cannot serve as a basis for enamels. An analysis of publications showed that no systematic research on aventurine enamels has been carried out. However, the authors are familiar with Chinese products decorated with green aventurine enamels and dating back to roughly the XVIII century.

The purpose of the present study was to obtain enamels with the aventurine effect. We used aluminoboron silicate glass with additives of tin, titanium, chromium, and copper oxides and fluorine ions. The glass was melted in porcelain crucibles of 25-g capacity in an electric furnace with silite heaters at a temperature of 1350°C for 30 min. The glass was then poured on a metal substrate. Enamels were applied to a tombac substrate using jewelry-enameling technology [5, 6]. The enamel firing temperature was 800°C, and the firing duration 3 – 5 min. The enamel-coating luster was 70%; the chemical resistance was graded as class A. The enamel had a dark green color. Both the enamel and the glass exhibited scintillating dots.

Having detected the aventurine effect in enamels of the system 80 (SiO_2 – B_2O – M_2O) – 20 (Al_2O_3 – SnO_2 – F^- – TiO_2 – Cr_2O_3 – Cu_2O), where M_2O is Na_2O + K_2O (Fig. 1), we attempted to clarify the nature of the resulting crystals in the glass, the effect of the glass composition on the quantity and size of the crystals contained in it, and the relationship between the degree of crystallization of the glass and the degree of crystallization of the enamel.

In spite of the crystallization of both the glass and the enamel, they are x-ray amorphous. Therefore, it is impossible to identify unequivocally the type of crystals. Figure 2 presents photographs of crystals contained in the glass and the enamel obtained with a Neophot-21 microscope. The

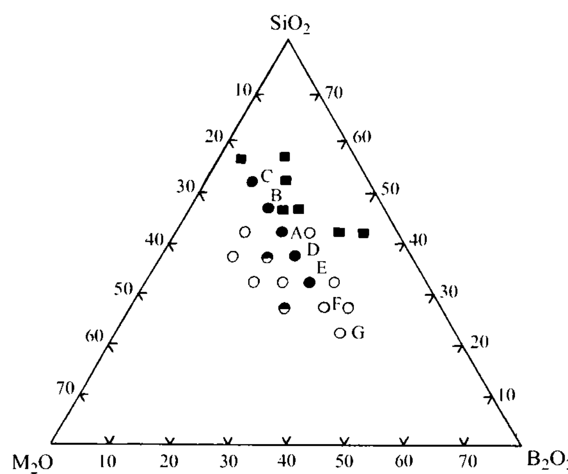

Fig. 1. Phase diagram of the compositions considered (A – G): ○) glass; ■) incompletely melted glass; ●) aventurine effect; ◓) weak aventurine effect.

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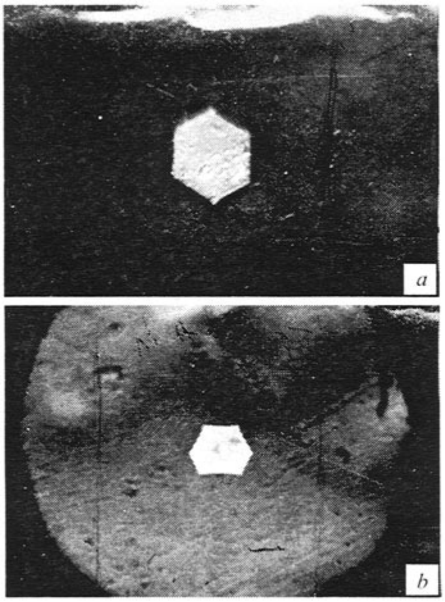

Fig. 2. Crystalline phase of aventurine glass A (a, × 200) and aventurine enamel (b, × 400).

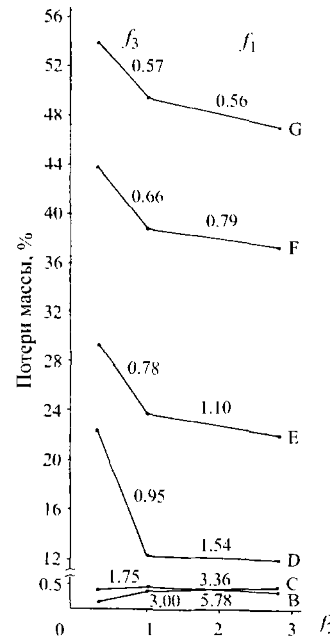

Fig. 3. Chemical resistance of the considered glasses as a function of the ratio $Na_2O : K_2O$.

glass itself is opacified (apparently, by titanium and tin oxides), but in a 0.5 mm chip it is virtually transparent, which makes it possible to observe individual crystals. The majority of the visible crystals have a hexagonal lamellar shape. They are clear, and underlying crystals are clearly visible beneath them. Both very small (4 μm) and relatively large (140 – 300 μm) crystals are encountered. In adding up to 7 wt.% chromium oxide, it can be assumed that crystals of fuchsite Cr_2O_3 are formed [7], since in the absence of chromium oxide in the glass composition, such crystals are not formed, although the glass remains opacified. It should be noted that the quantity and size of the crystals in the enamels are identical to the size and quantity of the crystals in the corresponding glass. Therefore, we investigated the effect of the glass composition on the size and quantity of the crystals contained in it.

The system 80 ($SiO_2 - B_2O_3 - M_2O$) – 20 ($Al_2O_3 - SnO_2 - F^- - TiO_2 - Cr_2O_3 - Cu_2O$) was investigated. In the concentration triangle (Fig. 1), the main compositions generating the aventurine effect are positioned on the line of constant composition of M_2O. The remaining compositions have a weak aventurine effect, and moreover, these glasses have a weak chemical resistance, and the enamels obtained from these glasses do not exhibit the aventurine effect.

The data on the chemical resistance (Fig. 3) show that the most resistant are glasses with the maximum possible quantity of silica (f_1 greater than 3).

The results obtained were analyzed with respect to the correlation of several factors f_1, f_2, and f_3: $f_1 = SiO_2 : (B_2O_3 + Al_2O_3)$, $f_2 = Na_2O : K_2O$, $f_3 = (Na_2O + K_2O) : B_2O_3$).

The most interesting is the correlation of the glass properties with the ratio f_2 of sodium oxide to potassium oxide under a constant total content of the alkali oxides. It is seen in Fig. 3 that f_2 affects the glasses in different ways. In glasses with a high silica content ($f_1 > 5$), an increase in f_2 from 0.36 to 2.83 produces a slight decrease in the chemical resistance. In glasses with $f_1 < 3.36$, another regularity is observed: an increase in f_2 substantially raises the chemical resistance of the glasses (and, accordingly, of the enamels).

An increase in f_2 from 0.36 to 2.83 sharply decreases the TCLE. For instance, the TCLE of glass E decreases from 100.2×10^{-7} to $90.6 \times 10^{-7}\ K^{-1}$, and for glass F from 98.7×10^{-7} to $85.3 \times 10^{-7}\ K^{-1}$. The effect of the factors f_1 and f_3 on this parameter is not as evident as in the case of the chemical resistance. It can be noted only that for $f_1 > 1.5$, the TCLE does not vary by more than $4 \times 10^{-7}\ K^{-1}$ (this is also true for $f_3 > 0.95$).

The quantity of crystals in the glass (and in the enamel) clearly correlates only with the factor f_2. An increase in f_2 from 0.36 to 2.83 on average doubles the number of crystals per unit surface area (glass B from 13 to 18, glass C from 12 to 20, glass D from 10 to 20, glass E from 9 to 19), but at the same time their size becomes smaller. Thus, in glasses C ($f_1 = 5.78, f_3 = 3.00$) the average crystal size decreases from 300 to 100 μm, and in glasses B ($f_1 = 3.36, f_3 = 1.75$) from 140 to 100 μm. In glasses D ($f_1 = 1.54, f_3 = 0.95$) no size variation related to the variation in f_2 is registered, while in glasses E ($f_1 = 1.10, f_3 = 0.78$), as f_2 increases, the crystal size increases from 40 to 120 μm.

Thus, using aluminoboron silicate glasses, it is possible to obtain aventurine enamels, when the content of SiO_2 is at least 37 wt.% and that of the alkali oxides is at least 20 wt.%.

The optimum ratio of sodium oxide to potassium oxide is equal to 3. The chromium oxide content should be at least 7%.

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